



Inhibitive Effect of Leaves Extract of *Coccinia Indica* on the Corrosion of Mild Steel in Hydrochloric Acid

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Abstract

The inhibitive effect of the acid extract of *Coccinia Indica* (CI) leaves on the corrosion of mild steel (MS) in hydrochloric acid medium was studied using weight loss and electrochemical methods. The inhibition efficiency increased with increase in concentration of the extract but decreased with rise in temperature. Furthermore, the inhibition efficiency synergistically increased on the addition of halide ions. Polarization measurement studies revealed that CI extract behaves as a mixed inhibitor. Physical adsorption mechanism is proposed from the trend in inhibition efficiency with the change in temperature and from thermodynamic parameters. It has been found that the adsorption of CI on MS complies with Langmuir and Temkin adsorption isotherms. FTIR confirmed the adsorption of CI on MS surface.

Keywords: Adsorption; Corrosion; Metals; Thermodynamic properties.

1. INTRODUCTION

Acid solutions are widely used in industries for lots of purposes, such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Due to the general aggressive nature of acid solutions, inhibitors are commonly used to reduce the corrosive attack of acid solutions of the contacted metallic materials, among which steel is the most extensively used (Gopi *et al.* 2010; Li and Mu 2005; Li *et al.* 2006). Corrosion inhibitors are usually added to the acid solutions to minimize metal loss and reduce acid consumption. However, most of the traditional inhibitors are synthetic compounds, which are expensive and easily lead to serious

environmental problems (Solomon *et al.* 2010; El-Etre, 2008; Torres *et al.* 2011). The development and application of corrosion inhibitors hence is focused on the inexpensive and environmental-friendly substances. The plant extracts thus emerge out as effective inhibitors of corrosion due to their low cost, high biodegradability, high availability and non-toxic nature (Da Rocha *et al.* 2010; Abiola *et al.* 2009). The objective of the present work is to investigate the inhibitive effect of acid extract of *Coccinia Indica* (CI) leaves on the corrosion of mild steel (MS) in hydrochloric acid medium using mass loss method, potentiodynamic polarisation and electrochemical impedance spectroscopy.

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2. EXPERIMENTAL

2.1 Materials

The experiments were performed with MS with the following composition.

wt % : C 0.143%, Ni 0.006%, Mo 0.018%, P 0.035%, Si 0.041%, Mn 0.271% and the rest is Fe. The aggressive solution of 1 M HCl was prepared by dilution of AR grade 37% HCl with distilled water. Fresh CI leaves were picked and then cleaned with tap water to eliminate ash and mud, dried in shade and then ground to powder. The acid extract was prepared by refluxing 10 g of dried and milled CI leaves in 500 ml of 1 M HCl for three hours and kept overnight for cooling. It was then filtered and the filtrate was stored in a standard flask. The desired concentrations of the inhibitor were prepared by diluting the above stock solution with distilled water.

2.2 Mass loss measurement

The MS sheet was cut into small pieces of dimensions $1 \times 5 \times 0.15$ cm and were abraded with a series of emery papers (grade 320-500-800), washed with distilled water, degreased with acetone and dried. After weighing accurately using digital balance with sensitivity of ± 0.1 mg, specimens in triplicate were immersed in the test solutions for specified periods of immersion in the absence and presence of CI extract. After a quantified interval of time the specimens were removed, rinsed with water, dried in warm air then stored in a desiccator and then reweighed to determine the weight loss. The percentage inhibition efficiency (%IE), corrosion rate (CR) and surface coverage (θ) were obtained using the following equations.

$$\text{CR (mpy)} = (K\Delta W) / (\rho A t) \quad (1)$$

$$(\% \text{IE}) = ((W_0 - W) / W_0) \times 100 \quad (2)$$

$$(\theta) = (W_0 - W) / W_0 \quad (3)$$

where, W_0 and W are the values of weight loss without and with inhibitor respectively. ΔW is the weight loss in gram, ρ is the density of coupon in g cm^{-3} , A is the area of coupon in cm^2 , t is the exposure period in hours.

2.3 Electrochemical measurements

The specimen with 7 cm long stem connected with clips for electrical conductance and mounted into cell to offer only one active flat surface having 0.9785 cm^2 surface area was exposed to the corrosive environment. Before each experiment, the electrode surface was cleaned with a sequence of emery papers of different grades (320-500-800), washed with distilled water and degreased with acetone. Electrochemical measurements, including potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were performed using CHI 604A model electrochemical analyser of CH instruments connected to a PC. A three electrode cell assembly consisting of a MS coupon of the mentioned dimension was used as working electrode (WE). A saturated calomel electrode (SCE) and a large-area platinum wire mesh were used as reference and auxiliary electrodes, respectively. All the experiments were performed in 100 ml of electrolytes under non-stirred and naturally aerated conditions. All the experiments were carried out at room temperature. Before each experiment, the electrode was permitted to corrode freely at its open-circuit potential (OCP). This steady-state OCP related to the corrosion potential (E_{corr}) of the working electrode. The polarization curves were obtained potentiodynamically between -0.250 and -0.750 V with the scan rate of 0.001 Vs^{-1} . The electrochemical impedance spectroscopy experiments were conducted in the frequency range of 100 kHz – 10 Hz at open circuit potential by applying alternating current signal of 0.005 V peak-to-peak.

The inhibition efficiency (% IE) from PDP curve were calculated by using the following equations,

$$(\% \text{IE}) = ((I_{\text{corr (b)}} - I_{\text{corr (i)}}) / I_{\text{corr (b)}}) \times 100 \quad (4)$$

$$(\% \text{ IE}) = ((R_p - R_{p(b)}) / R_p) \times 100 \quad (5)$$

where, $I_{\text{corr}(b)}$ is the corrosion current density in the absence of inhibitor. $I_{\text{corr}(i)}$ is the corrosion current density in the presence of inhibitor. R_p is the linear polarization resistance in the presence of inhibitor. $R_{p(b)}$ is the linear polarization resistance in the absence of inhibitor obtained from Tafel plots. The inhibition efficiency (% IE) from EIS was calculated by using the following equations,

$$(\% \text{ IE}) = ((R_{ct} - R_{ct(b)}) / R_{ct}) \times 100 \quad (6)$$

where, $R_{ct(b)}$ is the charge transfer resistance in the absence of inhibitor. R_{ct} is the charge transfer resistance in the presence of inhibitor obtained from the electrochemical impedance diagram.

2.4 FTIR

Fourier transform infrared (FTIR) spectra were recorded in Instant nam- SHIMADZU model- IR AFFINITY-1, using the KBr disk technique. The pure solid CI was mixed with KBr and made into a disk. The MS specimen after immersion (6 hours) in 1 M HCl with addition of CI at 27 °C for was cleaned with distilled water and then dried. The thin adsorption layer formed on steel surface was then scrubbed and the scrubbed material was mixed with a small amount of KBr powder in an agate mortar and made in to a KBr disk.

3. RESULTS & DISCUSSION

3.1 Weight loss measurements

Weight loss measurement is a non-electrochemical technique for the determination of corrosion rates (CR) and percentage inhibition efficiency (% IE). Table 1 show the % IE and CR for CI extract in 1 M HCl at room temperature (28 \pm 1). From the table, it is evident that the concentration of the inhibitor increase, the corrosion rate decrease and

the %IE increase. This indicates that the inhibitor molecules get adsorbed on the metal surface and prevent from the further corrosion. However addition of the inhibitors beyond certain concentration namely, 0.28% v/v of CI, the % IE decreases indicating desorption of the inhibitor molecule. For the present study, the reproducibility of experimental data was determined by the value of standard deviation. At every inhibitor concentration, the standard deviation value for either corrosion rate or % IE values are lower than 5%, which indicates the reproducibility of results obtained.

The immersion time is another important parameter which ascertains the inhibitive effect of the inhibitor on standing. In the present study, effect of immersion time (1–6h) on corrosion inhibition of CI in 1 M HCl at room temperature was investigated using weight loss method. From the Table 1 it is obvious that as the immersion time is increased from 1-6 h, the %IE values noted at all concentrations of CI increase up to 6 hours. These results demonstrate the formation of surface of film of the components of CI over the MS surface which get reinforced with immersion time.

The corrosion rates are observed to be lower in the inhibiting solutions containing extract–halide ions combination than that of the extract alone. The result obtained in the present study clearly show that the inhibition efficiency of the CI has enhanced considerably on the addition of halide ions and could be ascribed to a synergistic effect. The anodic dissolution of steel in aqueous solution is known to be significantly facilitated by hydroxyl ions that form intermediate catalytic complexes on the metal surface (Bockris *et al.* 1961).

Halide ions, at some concentrations, may replace hydroxyl ions adsorbed on the surface of the metal, thus leading to a reduction in the catalytic effect of the hydroxyl ions. The results reveal that the synergistic effect is more pronounced in the presence of I than Br than Cl⁻. The greater influence of the iodide ion is often attributed to its large ionic radius, high

hydrophobicity, and low electronegativity, compared to the other halide ions (Jeyaprabha *et al.* 2006).

3.2 Effect of temperature

Temperature can modify the interaction between mild steel and the acid in the absence and presence of the inhibitors. Gravimetric measurements were conducted in the temperature range of 303 K to 333 K in the absence and presence of various concentration of CI extract to study the influence of temperature on the corrosion behavior of mild steel. For each temperature the CR of MS decreased when the concentration of the extract increased. At high temperature the corrosion rate of MS increased more rapidly. At higher temperature the equilibrium shifted in such a way that the rate of desorption process is higher than that of the adsorption process.

In acidic solution the corrosion rate is related to temperature by Arrhenius equation, $\log CR = \log A - E_a / 2.303RT$ where, CR is determined from the weight loss measurement E_a the apparent activation energy, A the Arrhenius constant R the molar gas constant and T the absolute temperature. The apparent activation energy was determined from the slopes of $\log(CR)$ Vs $1/T$ and is presented in Table 2. It is clear that the values of E_a in the presence of the CI extract are higher than those in the uninhibited acid solution. These results are in accordance with the reported studies. The increase of E_a in the presence of inhibitor indicates the physical adsorption mechanism. The activation energies calculated for the inhibition of corrosion of mild steel are below 40 kJ/mol, which also supports the mechanism of physical adsorption. The exothermic nature of the adsorption process is indicated by the negative ΔH_{ads} values. The ΔS_{ads} values decreased with CI indicating the ordered arrangement in the presence of additives.

3.3 Adsorption isotherms

An adsorption isotherm gives the relation between the coverage of an interface with the adsorbed

species and the concentration of the species. Interpretation of the performance of the inhibitor can be enhanced by fitting the data in one of the known adsorption isotherms. Perfectly linear plot was obtained with Langmuir and Temkin isotherms.

3.4. Electrochemical measurements

3.4.1 Potentiodynamic Polarization Studies

Fig.1 represents the potentiodynamic polarization plots for MS in 1M HCl in the presence of

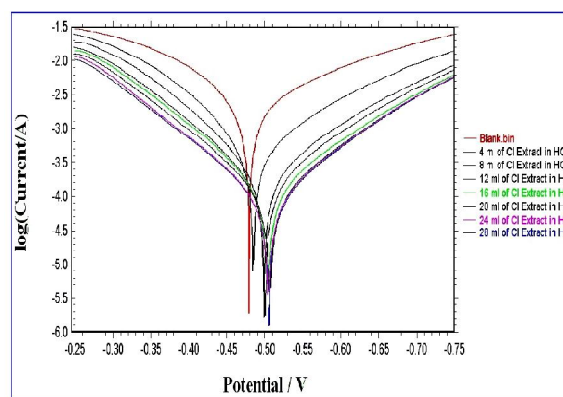


Fig. 1: Tafel plots for the corrosion of MS in the presence of CI

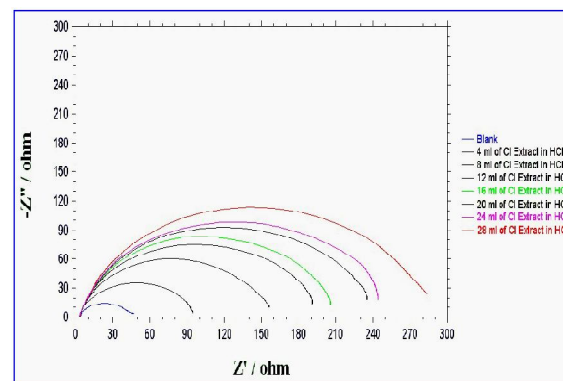


Fig. 2: Nyquist plots for the corrosion of MS in the presence of CI

Table 1. Influence of concentration of CI extract on the corrosion of MS in 1 M HCl

CI Conc. (% v/v)	1 hr		2 hrs		3hrs		4hrs		5hrs		6 hrs	
	CR (mgy)	IE (%)	CR (mgy)	IE (%)	CR (mgy)	IE (%)	CR (mgy)	IE (%)	CR (mgy)	IE (%)	CR (mgy)	IE (%)
Blank	178.80	-	130.83	-	106.12	-	145.81	-	146.53	-	140.27	-
0.2	162.47	29.27	58.87	55	44.25	58.22	45.98	68.16	44.48	68.71	43.61	69.43
0.4	117.74	34.15	53.42	59.17	36.89	64.38	39.13	70.56	38.38	73.01	34.53	74.61
0.6	10.30	43.90	53.18	60	36.34	65.75	32.71	76.53	32.27	77.30	26.89	80.83
0.8	89.25	51.22	50.15	61.67	29.07	72.60	30.53	78.03	30.53	78.52	21.80	84.45
1.0	82.86	53.66	47.97	63.33	24.71	76.71	26.92	82.02	25.89	82.82	16.72	88.08
1.2	65.41	60.98	43.61	66.67	23.26	77.40	22.89	84.27	23.55	84.66	13.81	90.16
1.4	52.33	73.17	32.71	75	20.35	80.82	20.17	85.02	18.32	87.12	10.90	92.23

Table 2. Values of E_a , ΔG_{ads} , ΔH_{ads} and ΔS_{ads} for various concentrations of the leaves extract of CI 1 M HCl

CI Conc. (% v/v)	E_a (kJ mol ⁻¹)	$-\Delta G_{ads}$ (kJ mol ⁻¹)				$-\Delta H_{ads}$ (kJ mol ⁻¹)	ΔS_{ads} (kJ mol ⁻¹)
		303 (K)	313 (K)	323 (K)	333 (K)		
Blank	43.83	-	-	-	-	-	-
0.2	46.99	11.4	11.6	10.3	11.6	18.35	0.02306
0.4	48.39	11.5	11.9	10.2	10.1	21.35	0.03293
0.6	49.55	11.8	12.1	10.9	10.8	21.04	0.03113
0.8	52.32	12.0	11.3	10.3	10.6	28.09	0.05344
1.0	52.44	11.9	11.4	10.6	10.5	22.26	0.03747
1.2	52.05	11.5	11.9	11.0	10.6	22.20	0.03495
1.4	52.64	12.1	11.8	11.1	10.8	25.25	0.04325

various concentrations of CI extract. The Tafel extrapolation and linear polarization methods were used to obtain the electrochemical parameters. The corrosion parameters viz. corrosion potential (E_{corr}), corrosion current density (I_{corr}), Tafel slopes (b_a & b_c) were derived from the polarization curves. The values of corrosion current density (I_{corr}) decreased with increase in concentration of CI extract. The inhibitor was first adsorbed onto the MS surface and impeded by merely blocking the reaction sites of the metal surface without affecting the anodic and cathodic reaction (Abdel Rehim et al. 2001.)

3.4.2 Electrochemical Impedance Spectroscopy

Fig.2 shows the Nyquist plots of mild steel corrosion in presence of CI extract. It is clear that CI extract acts profoundly as an excellent inhibitor to reduce acid corrosion of mild steel. The plots give the values of charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and % IE. The decrease in C_{dl} and increase in R_{ct} values with increase in concentration of CI extract indicates the adsorption of the compounds on the metal surface.

3.5 FTIR

FT-IR spectroscopic studies revealed that the phytochemical constituent of the plant extract were adsorbed on the surface resulting in the characteristic adsorption bands of the functional group in CI extract.

4. CONCLUSION

Extract of CI leaves were proved as promising inhibitors to protect MS from acid corrosion. The inhibition efficiency increased with increase in concentration of the extract but decreased with rise in temperature. Furthermore, the inhibition efficiency synergistically increased on the addition of halide ions. Polarization measurement studies revealed that CI extract behaves as a mixed inhibitor. Physical adsorption mechanism is proposed from the trend in inhibition efficiency with the change in temperature and from

thermodynamic parameters. The adsorption of CI on MS obeys Langmuir and Temkin adsorption isotherms. FTIR confirmed the adsorption of CI on MS surface.

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